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(54) PURIFICATION OF SULPHURIC ACID FROM MERCURY

(71) We, BOLIDEN AKTIEBOLAG, a Swedish Corporation, of Sturegatan 22, Stockholm, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for purifying sulphuric acid from mercury compounds dissolved therein.

More and more attention is being paid to the presence of mercury in industrial processes and the risks associated therewith. The presence of mercury in industrial processes presents serious problems, particularly in respect of processes producing such products as fertilizers and foodstuff. Sulphuric acid is used in very large quantities in the manufacture of these products, and therefore the content of mercury in the sulphuric acid must be low. Mercury can be introduced in process or product chains which have no direct association with the aforementioned products, thereby presenting serious contamination risks. One such product is the manufacture of hydrochloric acid and sodium sulphate from rock salt and sulphuric acid, the major portion of the mercury passing into the hydrochloric acid and via this acid to new processes and product.

Mercury containing sulphuric acid is liable to be obtained from sulphuric acid manufacturing plants based on the roasting of metal sulphides, for example pyrites or zinc blend when the roaster gas has not been sufficiently cleansed. Even when the gas is adequately cleansed, breakdowns in the operation of such plants may cause temporarily high contents of mercury to be introduced in the acid produced. This fact renders it necessary to purify mercury containing acids.

It is required of the acid purifying method that the sulphuric acid can be cleansed to low contents of residual mercury and that precipitated mercury-containing material can be removed from the acid. Further, the method should exclude the introduction of other toxic substances, such as lead and arsenic, into the acid. In certain instances, a rapid cleansing process is required, for example to restrict corrosion attack when purifying diluted acids.

It is known from German Patent No. 1 054 972 that dissolved mercury can be removed from concentrated sulphuric acid by treating the acid with minor quantities of certain metal sulphides, examples of such sulphides including PbS, As_2S_3, and Hgs. The best results are obtained with PbS, with which residual contents of mercury as low as <0.1 g/t acid are obtained. The dissolution of lead, occurring in the process, is considered to be of less importance, since the acid prior to being treated contains considerable quantities of, inter alia, lead originating from such apparatus as lead acid coolers in the absorption system. The separation of acid and solid material during the sulphide treatment process is assumed to take place by centrifuging or filtering techniques, optionally with a filter auxiliary agent, after a treatment time of 0.5 to 2 hours.

Concentrated sulphuric acid can also be cleansed with respect to mercury by treating the acid at 80 to 90°C with elementary sulphur having a particle size of 0.1 to 0.2 mm. The sulphur is removed from the acid after 1 to 2 hours, residual contents of mercury of the order of 5 to 10 g/t acid being obtained (USSR Patent No. 191 495; German Patent No. 1 216 263).

According to the German Patent No. 1 124 024, diluted sulphuric acid (according to the examples recited in the Patent 20-percent) can be cleansed from mercury dissolved therein by treating the acid with minor quantities of hydrogen sulphide or sulphides in the presence of active carbon. When putting this method into effect the acid, subsequent to adding the sulphide, is suitably passed through a bed of activated carbon with a contact time of 5 to 10 min., whereafter hydrogen peroxide is added to destroy residual quantities of sulphide and the acid passed to

a further bed of active carbon for a contact time of 3 to 6 mins. Residual mercury contents corresponding to <0.1 g/t concentrated acid have been shown.

In all of these cases it is obvious that sulphur answers for the removal of mercury from the solution. When treating sulphuric acid with sulphides or hydrogen sulphide, the reagent is decomposed to form elementary sulphur. The aforementioned patents do not disclose wherther mercury forms sulphides or is taken up on the surface of formed sulphur.

The present invention provides a method of purifying sulphuric acid from mercury comprising adding at least one thiosulphate to the sulphuric acid and separating the precipitated salts from the acid.

Thiosulphate is decomposed according to the formula

$$S_2O_3^{2-} \rightarrow SO_3^{2-} + S \qquad (1)$$

The sulphur formed herewith is at least initially almost colloidal and is very reactive, and thus has an extremely wide and active surface. After a while, the particles agglomerate into a particle size of up to 100 μm. This thiosulphate is suitably added in the form of an alkali metal salt.

Sulphur obtained by decomposing thiosulphate according to formula (1) in sulphuric acid is highly capable of taking up dissolved mercury from the acid. The precipitating effect is not limited to a small range of concentration and temperature, but can be effected with good effect at concentrations up to 95% H_2SO_4 but is preferably effected between 70 to 85% and at temperatures of between 10° and 100°C.

Mercury is precipitated from the sulphuric acid very rapidly, which means that it is possible to work with considerably low reaction volumes. The method was tested by cleaning 70% sulphuric acid containing 3.5 g of mercury per ton by adding 1 kg of thiosulphate per m^3. The test was carried out at a temperature of 100°C. The mercury content of the sulphuric acid had dropped to <0.1 g/t after only one minute.

Tests have been made which show that the residual mercury contents obtained in the acid after separation of the solid mercury containing substance by filtration under laboratory conditions is extremely low as soon as a minimum quantity of sulphur is formed. The quantity of sulphur formed naturally depends on the quantity of mercury in the acid and with the envisaged quantities of mercury up to 20 g/t may be as low as 0.04 kg/m^3 acid and as high as 10 kg/m^3 acid, although the quantity of thiosulphate used is preferably between 0.1—2 kg/m^3.

Tests have also shown that a sedimentation takes place very slowly with the small additions of thiosulphates (e.g. 0.1 to 1 kg/m^3 acid), although these quantities are sufficient for precipitating out the mercury. When larger quantities of thiosulphate are added, the precipitated sulphur flocculates or agglomerates to an extent depending upon the magnitude of the addition, which results to a more rapid sedimentation rate. Owing to the large quantities required to obtain a rapid sedimentation rate (5 to 10 kg thiosulphate/m^3) such a process does not afford a practical solution to the problem.

It has also surprisingly been found possible, however, that precipitated sulphur can be removed from sulphuric acid by flotation techniques, a sufficient flotation effect being obtained with solely foam builders. The flotation process, however, requires a foam builder having the necessary stability in the sulphuric acid in question. Satisfactory results have been obtained, for example, with commercially available foam builders, such as aminoacetates of the type marketed under the trade name Aminoacetate BG, Aminoacetate KK and Lilaflot (Registered Trade Mark) 810 and nonionic polyglycolethers, such as Berol (Registered Trade Mark) DIS-063, although the method of the invention is not restricted to these foam builders, but can be effected with any foam builder which does not decompose in sulphuric acid.

Neither does the method of the present invention require the use of other flotation reagents, such as collectors for example, when separating precipitated sulphur and sulphuric acid. The flotation process can be carried out with the use of known methods within the flotation technique, e.g. the injection of air under pressure through fine nozzles, the finely dividing of air by means of rotating agitators or the reduction in pressure in an air saturated volume of liquid. A particularly good effect is obtained by flotation with microbubbles of the type formed in the liquid when lowering the pressure in a gas saturated liquid mass, thereby also avoiding to a large extent movable components in the apparatus, which in turn facilitates the choice of construction material. When carrying out this type of flotation process, the whole of the liquid mass, or a minor portion of the same, can be saturated with gas under pressure. When using the method of the present invention it may be necessary to saturate the whole of the liquid mass within certain concentration ranges (around 70 to 80% H_2SO_4), where solubility in respect of the gas is low. If the purifying process is to carried out in conjunction with the dilution of sulphuric acid, the necessary quantity of air can be introduced by saturating the quantity of water required to dilute the acid with air. The flotation process may be effected in the presence of a conventional foaming agent in an amount of from 1 to 15 g/t acid, preferably from 2 to 5 g/t acid, or in the presence of

a conventional collector in an amount o ffrom 1 to 10 g/t acid.

The foam isolated by the flotation process and containing mercury-containing sulphur and sulphuric acid can be subjected to a further flotation process for enriching the mercury-containing material. Acid and mercury-containing material can also be separated by filtration, sedimentation or like techniques, which owing to the reduced volume can be effected much more simply than when required to treat the whole quantity of acid concerned. The finely isolated mercury-containing sulphur can be destroyed by burning under conditions which permit mercury to be removed from the gases of combustion, for example in a sulphur pyrites roasting furnace, followed by an effective roaster gas purifying system.

By combining the precipitation of mercury on extremely finely divided (colloidal) elementary sulphur, obtained by decomposing thiosulphate, and the removal of the very difficulty separated precipitate by flotation, suitably effected with solely foam builders and in a flotation apparatus lacking movable components, a generally useable sulphuric acid purifying method has been obtained. The precipitation and separation rates are rapid and can be adapted without difficulty for purifying large quantities of acid.

As before mentioned, the mercury-containing solid material can also be separated by filtering the acid through a filter press constructed of acid-proof material. Naturally, other separating apparatus, such as filtering centrifuges capable of resisting attack by acid can be used.

The process of the present invention will be further described with reference to the following illustrative examples.

Example 1

Sulphuric acid was cleansed of mercury on a laboratory scale, by adding 1 g of sodiumthiosulphate ($Na_2S_2O_3 . 5H_2O$) and 1 g of a nonionic foam builder (fatty alcohol polyglycolether Berol DIS-063) per liter of acid to sulphuric acid having a concentration of 85% and containing 3.5 g Hg/t.

Air was then injected into the acid through a fine-pore glass filter at 20°C and at 70°C. In both cases a foam containing mercury-containing elementary sulphur and sulphuric acid was isolated after 50 minutes. At 20°C, the quantity of sulphuric acid in the foam was found to be approximately 15% of the total quantity, while the purified acid had a mercury content of 0.85 g/t. At 70°C the corresponding values were 10% and 1.2 g/t.

Example 2

When manufacturing phosphoric acid for fertilizing purposes, sulphuric acid is used in a quantity corresponding to approximately 20 t of H_2SO_4/hour. Prior to being used, it was necessary to dilute the acid to approximately 70% H_2SO_4 and to cool the same to approximately 40°C. Owing to the comparatively high mercury content (2—4 g/t) of the sulphuric acid, it was necessary to effect a mercury purifying process.

In this instance it was found suitable to divide the diluting process into two stages: in a first step the acid was diluted from 95% to approximately 80% H_2SO_4, whereafter the acid mixture was cooled to approximately 35°C.

0.5 kg sodiumthiosulphate ($Na_2S_2O_3.5H_2O$) and 3 g of aminoacetate was added to the cooled acid per m^3 acid. Immediately after admixing the aforementioned substances, i.e. in practice approximately 1 minute afterwards, the remaining diluting water was added, this water having been saturated with air at a pressure of 5 atm. The temperatures was then raised approximately 5°C and air released in the form of very small bubbles, which carried precipitated mercury-containing sulphur to the surface. The flotation process was carried out in a rectangular tank having an area of approximately 4 m^2, the 80% acid and remaining diluting water being charged to one short side of the tank and the foam and purified acid departing at the other short side thereof.

The purified acid was used to manufacture phosphoric acid while the foam was collected and broken down. The mixture of pure sulphuric acid and mercury-containing sulphur obtained hereby was destroyed in a pyrites roasting furnace, mercury being reintroduced into the gas purifying system, thereby preventing the mercury from constituting an emission risk.

By means of this process, the mercury content of the sulphuric acid was reduced from 2—4 g/t to <0.5 g/t by adding only minor quantities of sodium thiosulphate to the acid and no other contaminants. The purifying process was carried out in apparatus completely lacking in movable parts, and consequently when constructing the apparatus it was possible to select the construction material totally with respect to the risk of chemical attack, which is high in 70% acid, while the mechanical strength of the parts was of less interest. Since the process of the present invention can be effected rapidly, the relatively large flow of acid can be purified in apparatus requiring but small space.

Example 3

Mercury-containing sulphuric acid was purified from mercury in a plant for the manufacture of sulphuric acid, including the roasting of mercury containing sulphidic minerals, the purification of formed mercury and SO_2-containing roaster gases and the drying of the roaster gases in a drying tower,

by charging the mercury-containing sulphuric acid to a system for circulating sulphuric acid used for drying the moist roaster gas. It was found that the mercury present in the roaster gas was absorbed in the acid, owing to the fact that the acid containing mercury in divalent form. The sulphuric acid contained 25 mg Hg/kg and the gas contained 5.7 mg Hg/kg. The acid was charged to the circulation system in a quantity of 15 tons/hr at a concentration of 90% and 19 tons of acid with a concentration of 70% were withdrawn from the system each hour. The system was thus in balance. The withdrawn acid was passed to an aqueous solution of sodium thiosulphate in a quantity corresponding to 3 kg of $Na_2S_2O_3 . 5H_2O$ per m^3 of acid in a precipitation tank capable of accommodating 20 tons of sulphuric acid. The sulphuric acid was passed from the precipitation tank to a filter press, where precipitated mercury was separated from the acid. The mercury content of the filtered acid was found to be 0.2 mg/kg, representing a 99% purification. Mercury was also removed from the gas at the same time. After removing substantially all moisture from the gas, the gas was found to contain 0.5 mg/m^3 of mercury. The gas was then finally dried in a second drying tower, to which 3 tons of 95% mercury-containing acid were passed per hour in a circulating system. Approximately 3 tons of sulphuric acid were removed each hour from the circulating system and admixed with the acid withdrawn from the first drying tower. The mercury content of the gas was, in this way, lowered to <0.1 mg/m^3.

WHAT WE CLAIM IS:—

1. A method of purifying sulphuric acid from mercury comprising adding at least one thiosulphate to the sulphuric acid and separating the precipitated solids from the acid.

2. A method as claimed in Claim 1 wherein the thiosulphate is added to the acid in an amount of from 0.04 to 10 kg/m^3 acid.

3. A method as claimed in Claim 2 wherein sodium thiosulphate is added to the acid in an aqueous solution of the thiosulphate in an amount of from 0.1 to 2 kg/m^3 acid.

4. A method as claimed in any of Claims 1 to 3 wherein the mercury is precipitated out at a temperature of from 10 to 100°C.

5. A method as claimed in any of Claims 1 to 4 wherein the sulphuric acid has a concentration of up to 95% by weight.

6. A method as claimed in Claim 5 wherein the sulphuric acid has a concentration of from 70 to 85% by weight.

7. A method as claimed in any of Claims 1 to 6 wherein the precipitated solids are separated from the acid by flotation, centrifuging or filtration.

8. A method as claimed in Claim 7 wherein the quantity of air required for the flotation process is supplied by saturating the acid or a subsequently admixed quantity of acid or water used to dilute the acid with air under pressure.

9. A method as claimed in Claim 8 comprising injecting into the acid the quantity of air required for the flotation process.

10. A method as claimed in any of Claims 7 to 9 wherein the flotation process is effected in the presence of a conventional foaming agent in an amount of from 1 to 15 g/t acid.

11. A method as claimed in Claim 10 wherein the foaming agent is in an amount of from 2 to 5 g/t acid.

12. A method as claimed in any of Claims 7 to 9 wherein the flotation process is effected in the presence of a conventional collector in an amount of from 1 to 10 g/t acid.

13. A method of purifying sulphuric acid from mercury substantially as herein described with reference to any of the foregoing examples.

14. Sulphuric acid when purified by the method as claimed in any of Claims 1 to 13.

15. Mercury when separated from sulphuric acid by the method as claimed in any of Claims 1 to 13.

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